Recovery of Precious Metals From Space

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ABSTRACT

The overall objective of this project is to develop efficient and economical separation and recovery methods for the platinum group and other precious metals. The separation of Pd(II) from Pt(II), Ir(III) and Rh(III) with trioctylphosphine oxide (TOPO) in heptane using centrifugal partition chromatography (CPC) has been investigated for the first time. Activities to achieve this objective to date have focussed on selection and evaluation of extraction systems for the PGM and modification of selected systems for multistage operation with a view to scaling up to desired macro levels. On the basis of preliminary evaluation of a series of simple metal complexing agents and chelating agents, the trioctylphosphine oxide (TOPO) in heptane was selected as a likely system for isolating of Pd(II) and Pt(II) from the other PGM. A novel multistage apparatus capable of configuration as a simple rugged device, called centrifugal partition chromatograph (CPC) was shown to be effective. The extraction of Pd(II) has been studied by CPC and batch solvent extraction. The distribution ratios for Pd(II) determined by both methods agree well. In low HCl concentrations (<0.1 M), the extracted species was

$PdCl_2.(TOPO)_2$, irrespective of the chloride concentration, while at acid concentrations above 0.1 M, the Pd was extracted as the ion pair, $2(TOPO.H^+).PdCl_4^{2-}$. Base line separation of Pd(II) and Pt(II) in CPC was obtained under a variety of chloride and HCl concentration with the average number of theoretical plates being 390 $\pm$ 40 at a flow rate of 0.47 $\pm$ 0.05 mL/min. It was demonstrated that the efficiency of CPC for metal separation was limited by chemical kinetic factors rather than instrumental factors, strongly suggesting that dramatic improvements (up to 1300 theoretical plates, achieved with simple organic distribuends) can be achieved by studying reaction kinetics of formation and dissociation of the extractable metal complex.

INTRODUCTION

The separation of platinum group metals, while widely investigated, continues to pose challenges (1,2). Ion pair extractions of the chloro anions are reasonably rapid but not so selective. Extraction as chelates are more selective but these have very slow formation/dissociation kinetics. The selectivity problem can be addressed by the use of multistage methods.

The separation of platinum group metals by multistage methods, namely, extraction chromatography has been previously attempted (3). This process in which, an organophosphorus reagent was loaded on a silica solid support, was tedious and difficult, and the efficiency of separation and resolution of the individual elements was not good. Further, the coated extractant leached from the solid support. In this laboratory, the approach has involved the use of multistage solvent extraction using the principle of countercurrent distribution as well as the use of derivatized supports which would avoid the problem of reagent leaching (4). Another possible approach is centrifugal partition chromatography (CPC). CPC is based on the principle of counter current distribution (5). Two immiscible phases, namely, an organic phase like heptane containing an extractant and an aqueous phase at the appropriate pH are used. One phase is held stationary in cartridges by the action of centrifugal force and the other phase is pumped through the stationary phase, achieving multistage solvent extraction. An analyte

mixture is injected into the CPC and the "chromatogram" of the separated components is obtained using a UV-VIS detector. The chromatogram can be analyzed by the usual equations (6). This technique has been widely applied for the separation of natural products (7). There have been a few attempts to separate metal ions, like lanthanides (8,9). These attempts generally had poor column efficiencies and incomplete resolutions of the analyte components. We have recently demonstrated a much improved analytical scale separation of adjacent lanthanides (10). Complete base line separation of adjacent lanthanides were achieved with a column efficiency of 320 $\pm$ 40 plates while the best previous efficiency was about 50 plates (10). Described here are our results for the separation of Pd(II) from Pt(II), Ir(III) and Rh(III) by CPC using TOPO as the extractant, selected from examination of organophosphorus reagents which show promise for the extraction separation of platinum group metals (1,3).

EXPERIMENTAL

Reagent

TOPO (>99% purity, Aldrich), was used as received. All other reagents were of analytical grade. Metal free heptane and water solutions were equilibrated overnight before being used in CPC experiments. Palladium, platinum, iridium and rhodium stock solutions of 10^{-2} M were prepared by dissolving a weighed quantity of palladium(II) chloride (59.9% Pd, Alfa Products), sodium tetrachloro platinum(II) (44.3% Pt, Johnson Mathey, Inc.), sodium hexachloroiridium(III) (36.0% Ir, Alfa Product) and Rhodium(III) chloride trihydrate (39.0% Rh, Aldrich Chemical Company, Inc.) in 10^{-2} M HCl solution. Deionized-distilled water was used throughout this study.

Apparatus & Procedure

CPC experiments were performed with a Sanki, Co., Japan assembly consisting of a model SPL centrifuge containing 6 analytical/semi-preparative cartridges each having 400 channels (2400 total channels), a model CPC FCU-V loop injector and a model LBP-V pump. CPC experiments were conducted with 0.1 M TOPO in heptane as the stationary phase and water at the appropriate pH and chloride (using NaCl) concentration as the mobile phase, pumped in the descending mode. Equilibration of the two phases at 800 rpm and 25 °C provided 22 mL of heptane and 110 mL of water. A UV-VIS spectrophotometric detector (model 770, Schoeffel Instrument Co.) with a 0.1 mL cell volume of 8 mm path length was used, which was set at 238 nm. Data was acquired every 20 seconds using a IBM/PC interfaced to the detector. One mL
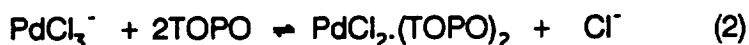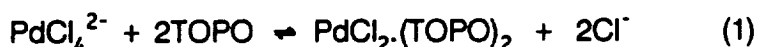
of a mixture of the metals was injected into the CPC for a single run. Flow rates between 0.5 and 2 mL/min. were used in these experiments.

Single stage solvent extractions were carried out by shaking equal volumes (10 mL) of heptane containing TOPO with an aqueous phase containing $4X10^{-4}$ M Pd in a glass vial with a box type Eberbach shaker. Determination of the distribution ratios (D) of Pd(II) as a function of time indicated that equilibrium was achieved within 5 minutes or less, depending on the chloride and TOPO concentrations. The heptane-aqueous mixtures were equilibrated for one hour to ensure complete equilibrium. The aqueous Pd concentration was determined using an ICP-AES (model 6500, Perkin-Elmer Co., USA) at its most sensitive wavelength, 340.458 nm (detection limit = 1.2 ppm). Standard solutions of Pd (10, 20, 30, and 40 ppm) were prepared daily for calibration in the same matrix as sample to eliminate all matrix effects. All pH measurements were made with an Accumet pH meter (model 925) which was calibrated daily with standard buffer solutions.

RESULTS AND DISCUSSION

Extraction Equilibria of Pd(II) Species by Solvent Extraction and CPC

The chloro-palladium species extracted is a function of chloride concentration (Figure 1) (11). The extraction equilibria of Pd(II) species were characterized by both solvent extraction and CPC as a function of chloride and TOPO concentrations. The extraction equilibria were inferred from the dependence of log D_{Pd} on log [Cl$^-$] and log [TOPO], namely from the slopes of these plots (12). These equilibria are:

$$PdCl_4^{2-} + 2TOPO \rightleftharpoons PdCl_2.(TOPO)_2 + 2Cl^- \qquad (1)$$

$$PdCl_3^- + 2TOPO \rightleftharpoons PdCl_2.(TOPO)_2 + Cl^- \qquad (2)$$

$$PdCl_2 + 2TOPO \rightleftharpoons PdCl_2.(TOPO)_2 \qquad (3)$$

The extraction equilibrium constants for each Pd species can be calculated by using the equilibrium expressions:

$$Log\ K_{ex.4} = Log\ D_{Pd} + 2Log[Cl^-] - 2Log[TOPO] - Log\alpha_4 \qquad (4)$$

$$Log\ K_{ex.3} = Log\ D_{Pd} + Log\ [Cl^-] - 2Log[TOPO] - Log\alpha_3 \qquad (5)$$

$$Log\ K_{ex.2} = Log\ D_{Pd} - 2Log[TOPO] - Log\alpha_2 \qquad (6)$$

where α_4, α_3, and α_2 are the fraction of each Pd species, $PdCl_4^{2-}$, $PdCl_3^-$, and $PdCl_2$, respectively
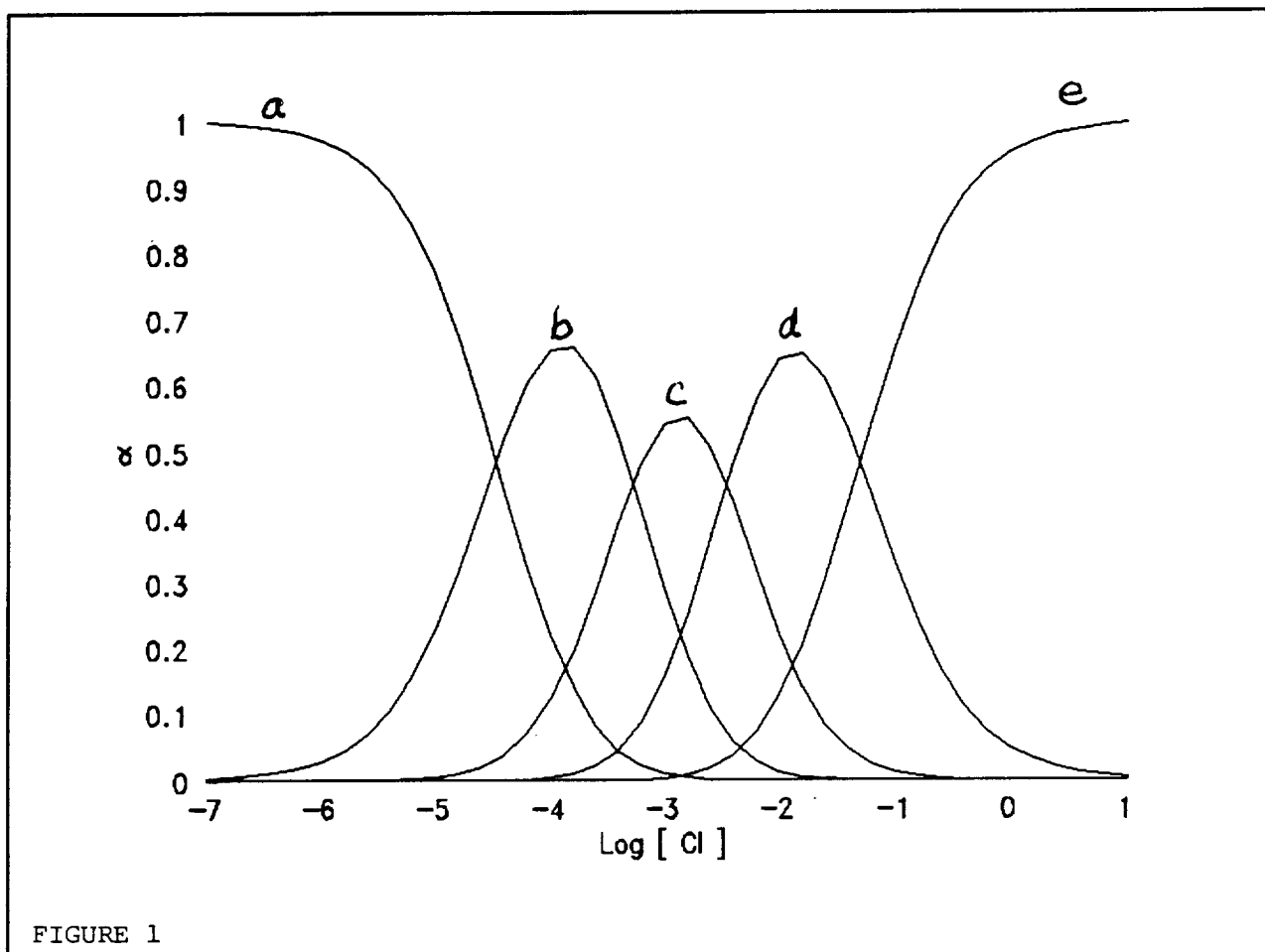
FIGURE 1

in aqueous phase as shown in Figure 1.

Plots of Log D_{Pd} VS Log [TOPO] at 10^{-3} M and 0.1 M [Cl$^-$] yielded a slopes of 1.89 and 1.88, respectively (Figure 2). This indicates that each Pd species is bound to 2 TOPO. A similar plot of Log D_{Pd} - Log α_n of each Pd species as a function of Log [Cl$^-$] yielded slopes of -1.97, -0.97, and 0.003 were obtained for $PdCl_4^{2-}$, $PdCl_3^-$, and $PdCl_2$ species respectively. These indicate the number of chloride ions released from $PdCl_4^{2-}$, $PdCl_3^-$, and $PdCl_2$ species to be 2, 1, and 0 respectively (equations 1-3).

The extraction constants, $K_{ex.4}$, $K_{ex.3}$ and $K_{ex.2}$, can be calculated from equation 4, 5 and 6 to be 0.14, 2.75 M^{-1}, and 794.3 M^{-2} respectively (Table 1). This $K_{ex.2}$ value is smaller by about
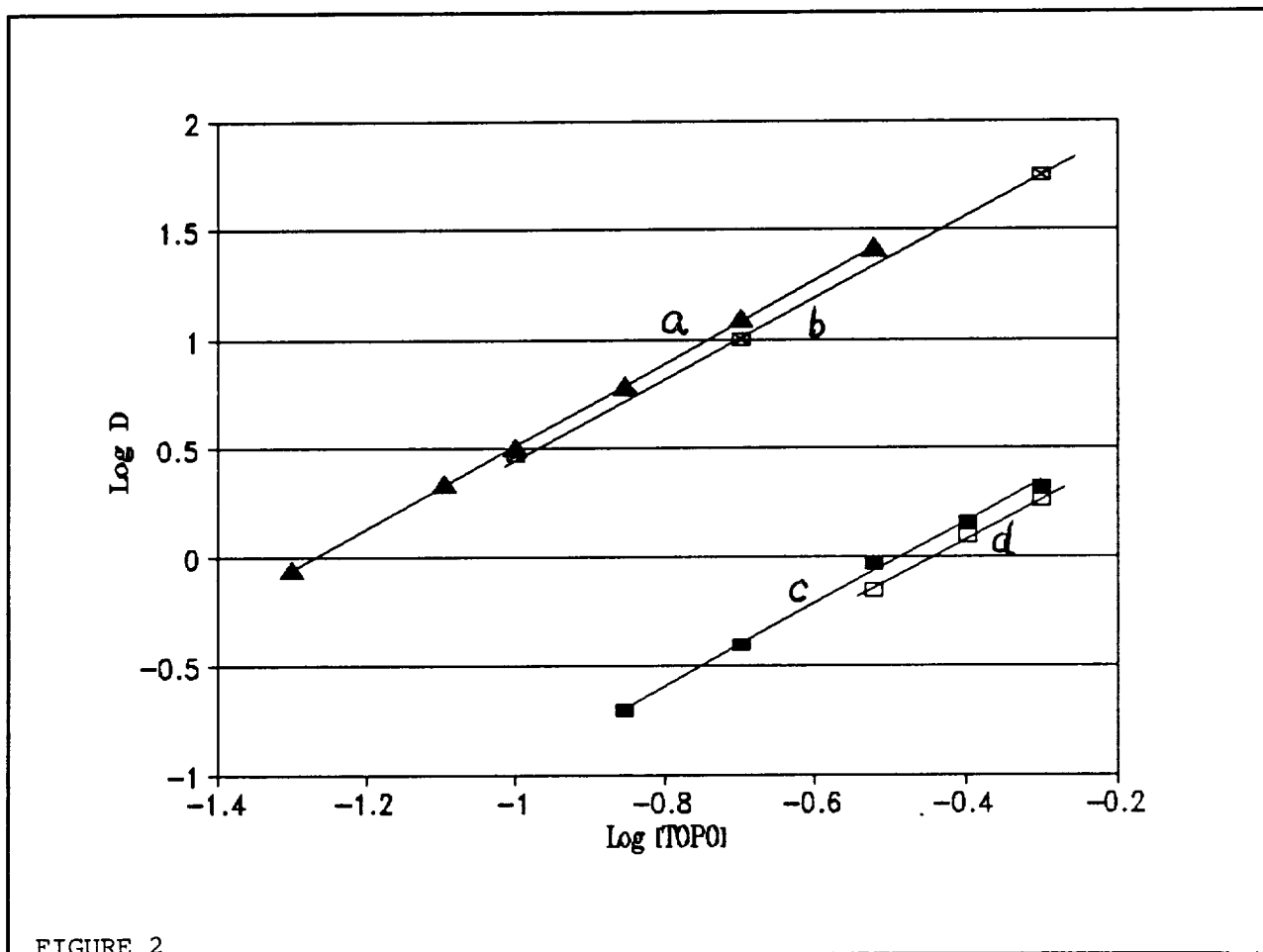
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FIGURE 2

5 orders of magnitude compared to the $K_{ex.2}$ value for the extraction of $PdCl_2$ by R_2 S (2), as expected for a harder ligand.

TABLE 1. Equilibrium Data for Extraction of Palladium by TOPO.

A. Dependence on [TOPO].

Pd(II) = 4×10^{-4}, [Cl⁻] = 0.1, pH = 3

[TOPO],M	Log D	Log $K_{ex.2}$ (α_2=0.011)	Log $K_{ex.3}$ (α_3=0.330)	Log $K_{ex.4}$ (α_4=0.658)
0.50	0.32	2.86	0.40	-0.8
0.40	0.16	2.89	0.43	-0.86
0.30	-0.03	2.95	0.49	-0.80
0.20	-0.39	2.94	0.47	-0.82

| 0.14 | -0.71 | 2.93 | 0.48 | -0.81 |

TABLE 1. Equilibrium Data for Extraction of Palladium by TOPO.   B.
Dependence on [Cl-]

$Pd(II) = 4 \times 10^{-4}$ M, [TOPO] = 0.5 M, pH = 3

[Cl⁻],M	Log D	Log Kex.2	Log $K_{ex.3}$	Log $K_{ex.4}$
0.10	0.32	2.86	0.40	-0.89
0.14	0.08	2.87	0.41	-0.88
0.20	-0.19	2.87	0.41	-0.88
0.30	-0.52	2.86	0.40	-0.89
0.40	-0.72	2.89	0.43	-0.86
0.50	-0.92	2.88	0.42	-0.87

The comparison of distribution ratios (D) determined by single stage batch solvent extraction and by CPC are also shown in Figure 2. The data from two methods are well in agreement within experimental error. The D values from CPC experiments were obtained by the following equation:

$$V_r = V_m + DV_s \tag{7}$$

where V_r = retention volume of sample

V_m = mobile phase volume or dead volume

V_s = stationary phase volume

Extraction at High Acid Concentration

We have found that TOPO can be protonated at higher HCl concentration, and the protonated TOPO can extract $PdCl_4^{2-}$. These experiment were carried out at 1 M HCl where the $PdCl_4^{2-}$ is the predominant species (99.50%). The dependence of log D_{Pd} on log [TOPO] and log [H⁺] yielded the slopes of 2.01 and 1.95 respectively D_{Pd} was also independent of chloride concentration, leading to the overall equilibrium in equation 8.

$$PdCl_4^{2-} + 2TOPO + 2H^+ \rightleftharpoons 2(TOPO.H^+).PdCl_4^{2-} \tag{8}$$
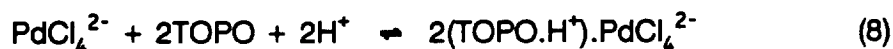
The equilibrium constant, $K'_{ex.4}$, can be calculated from the following equation:

$$\text{Log } K'_{ex.4} = \text{Log } D_{Pd} - 2\text{Log[TOPO]} - 2\text{Log[H}^+] - \text{Log } \alpha_4 \qquad (9)$$

where α_4 is very close to unity as evident from Figure 1.

The determination of the equilibrium constant, $K'_{ex.4}$, by varying the concentration of either TOPO or acid is 93.3 M^{-4}. This $K'_{ex.4}$ value is smaller than $K_{ex.2}$ (794.3 M^{-2}) but larger than $K_{ex.4}$ (0.14), the equilibrium constants for the extraction of $PdCl_2$ and $PdCl_4^{2-}$ by protonated TOPO. This indicates that $PdCl_4^{2-}$ is more efficiently extracted by protonated TOPO than by neutral TOPO.

Separation of Pd from Pt, Ir and Rh using CPC

CPC experiments were conducted at pH = 3 and 10^{-3} M [Cl$^-$]. Experiments were not carried out at lower pH to avoid corrosion or damage to the instrument. The distribution ratio of Pt is very small under these conditions. The Pt peak in the chromatogram always appeared at a position close to the chloride peak (dead volume peak). The degree of separation of two peaks is defined as resolution, R_s, determined by the following expression:

$$R_s = 2d / (W_A + W_B) \qquad (10)$$

where d is the distance between the peak maxima and W is width of each peak. The larger the resolution, the better the separation. The separation of Pd from Pt in Figure 4 shows base line separation of Pt and Pd with a resolution of 1.54 or < 0.3 % peak overlap. The retention volumes (R) of Pt and Pd are 110 mL and 135 mL respectively. The equation for countercurrent distribution together with the D values of Pt and Pd from the experiment in Figure 4 ($D_{Pt}=0.11$, $D_{Pd}=1.4$ and N=360) can be used to simulate the chromatogram.

The fraction, F_o, of a given analyte with a distribution ratio, D, in the organic phase where the ratio of the volume of the organic phase to the volume of the aqueous phase is R_v is given by the following equation:

$$F_o = DR_v / (DR_v + 1) \qquad (11)$$

In a countercurrent distribution involving N stages,
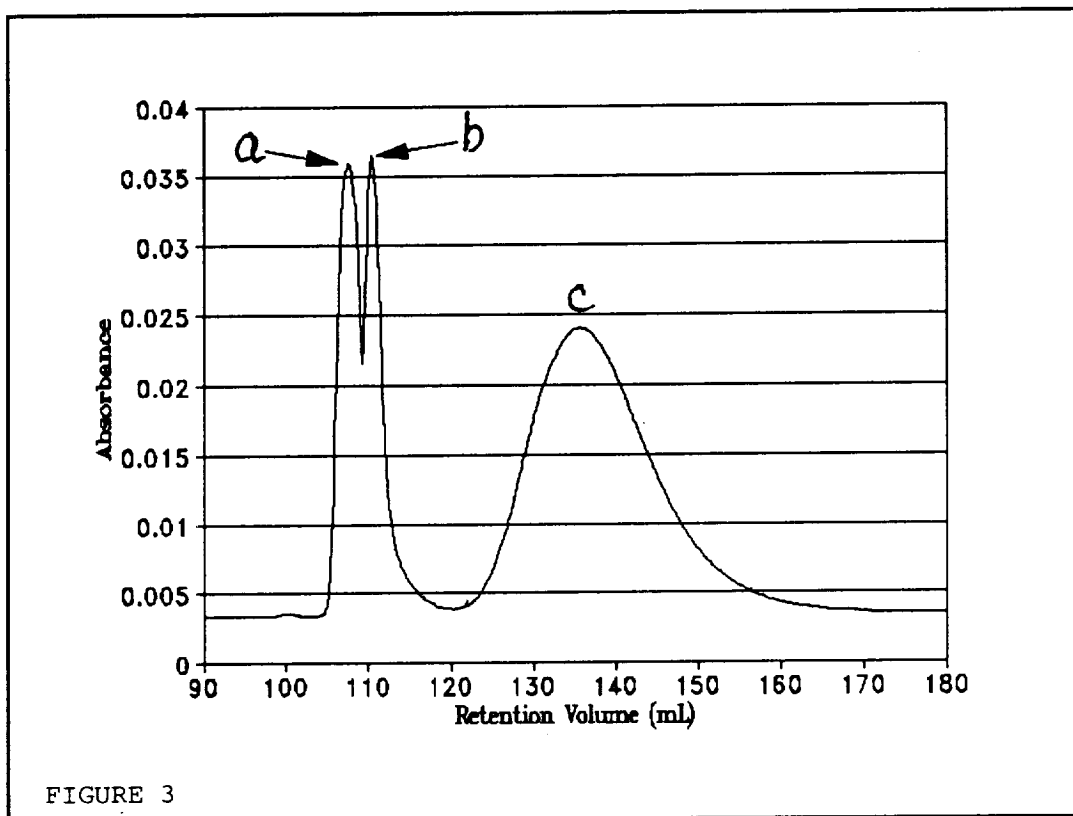
$$(F_o + F_w)^N = 1 \qquad (12)$$

FIGURE 3

where F_w is the fraction of the analyte, and C_m, its concentration in the aqueous phase. The concentration of the analyte in the mth stage of the separation is given by

$$C_m = [N!/m!/(N-m)!] \, F_o^{N-m} \, F_w^m. \qquad (13)$$

The computer-simulated chromatogram shows the R values of both Pt and Pd corresponding to the experiment, 111 mL and 134 mL respectively (Figure 5). Figure 6 shows the base line separation of Pd from the other platinum group metals (Pt, Ir, and Rh). It may be seen that partial resolution of Pt(II) from Ir(III) and Rh(III) was obtained under these conditions. However, complete separation of the four platinum group metals was not possible using TOPO.

The efficiency of CPC is determined by the number of theoretical plates (N) and can also be expressed as a number of channels per plate by dividing the total number of channels (2400) by N. The N of the column is calculated by the ratio of the elution volume, V_r, and the band width, W, as in equation 14.
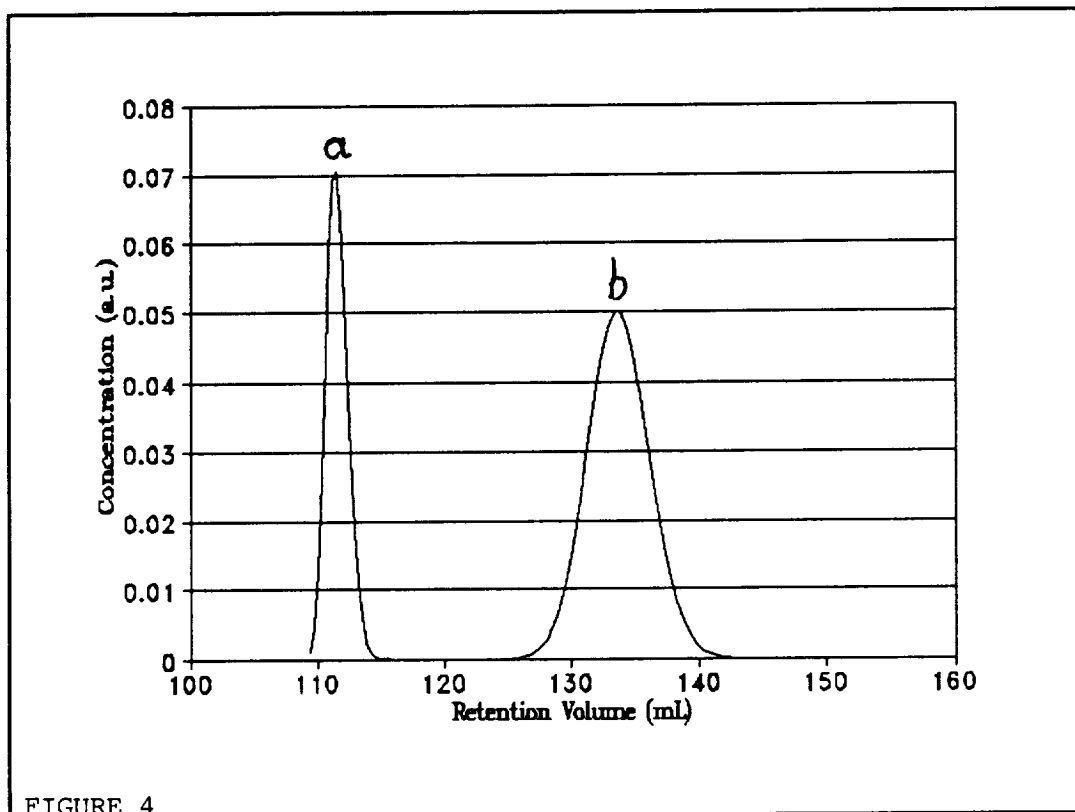
FIGURE 4

$$N = 16(V_r/W)^2 \qquad (14)$$

Effect of Flow Rate on Column Efficiency

The column efficiency decreased as the flow rate was increased from 0.5 mL/min. to 3 mL/min. The number of channels/theoretical plate increased with flow rate as shown in Figure 7. This Van Deemter type plot is similar to those observed in HPLC experiments and opposite to that observed for the separation of organic compounds by CPC using two immiscible organic solvents (6). The same behavior was observed for the CPC separation of lanthanides by cyanex 272 (10). The maximum column efficiency in the separation of Pd(II) from Pt(II) was 390 $\pm$ 40 at 0.47 mL/min, which is about the same as that observed in lanthanide separation (10). The factors affecting CPC column efficiency in separation of simple organic distribuends are much more similar to those encountered in traditional liquid chromatography. For example, γ-picoline with retention characteristics similar to Pd(II) indicated CPC efficiency of 1220 theoretical plates. Obviously, chemical kinetic factors in extractable complex

formation and/or dissociation limit the observed number of theoretical plates. This strongly suggests the value of a study of kinetics which is now in progress.
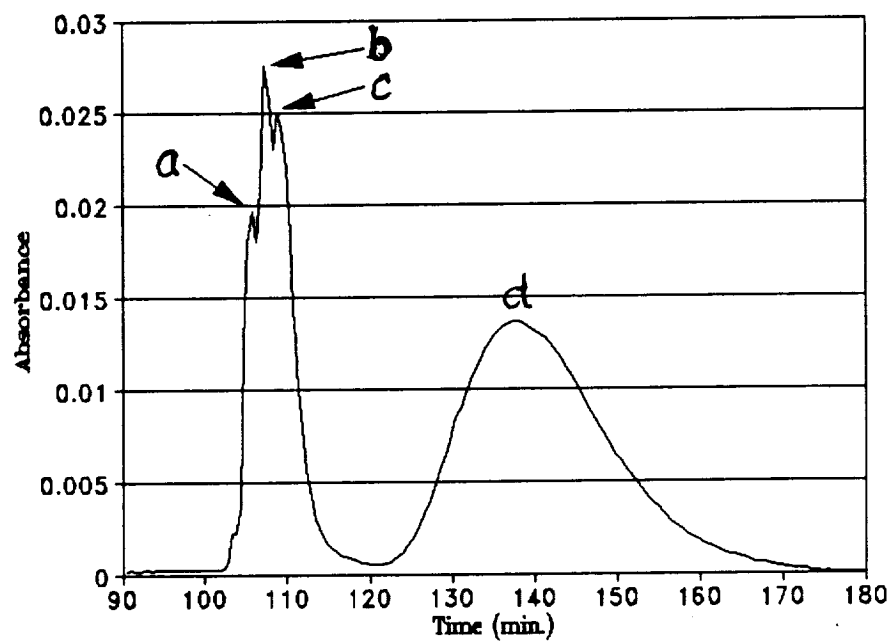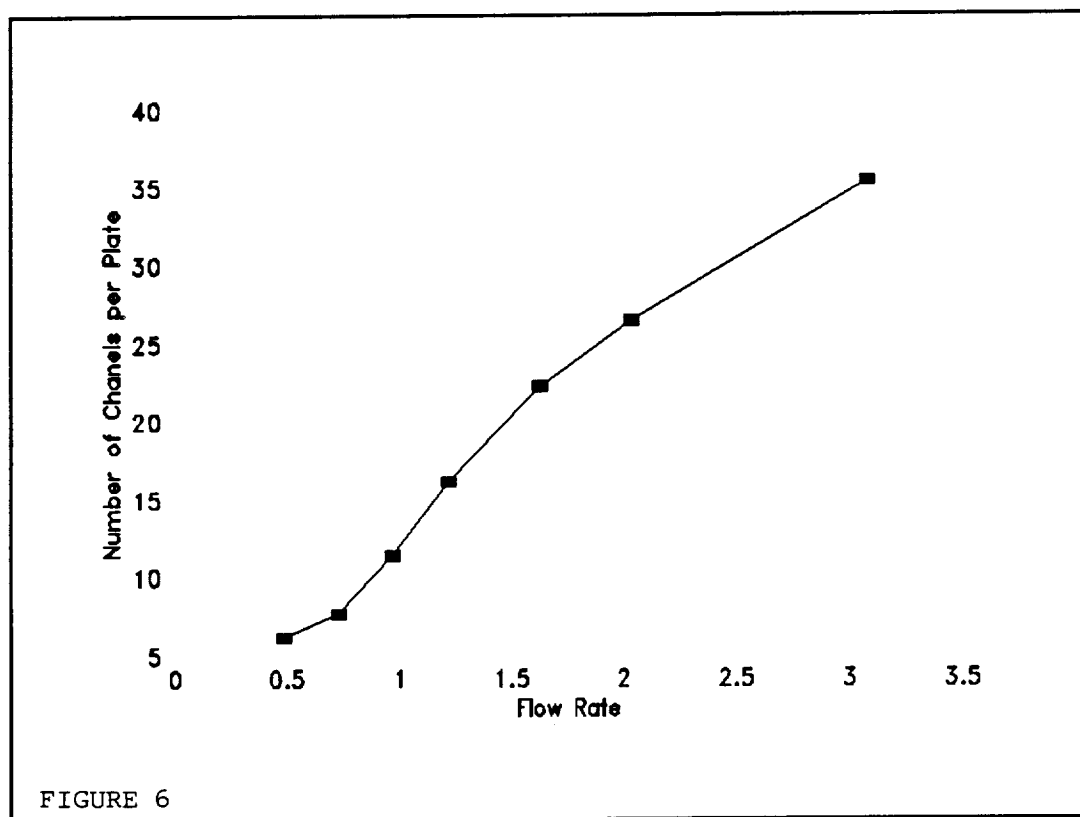

FIGURE 5

FIGURE 6

CONCLUSIONS

We have shown that Pd(II) can be completely separated from Pt(II), Ir(III) and Rh(III) using CPC under a variety of conditions using TOPO. We have been able to partially separate Pt(II) from Ir(III) and Rh(III). This illustrates the usefulness of the multistage solvent extraction technique, CPC. The nature of the species extracted and the extraction equilibrium constants for Pd(II) extraction by TOPO have been determined under a variety of condition using batch solvent extraction experiment and CPC. The results from batch solvent extraction an CPC agree well and indicate that $PdCl_2$ has the best extractibility among the various Pd(II)-chloro complexes.

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FIGURE CAPTIONS

FIGURE 1.   The Pd(II)-chloro species as a function of chloride concentration, a) Pd, b)$PdCl^+$, c)$PdCl_2$, d) $PdCl_3^-$ and e)$PdCl_4^{2-}$.

FIGURE 2.   Dependence of log D as a function of log [TOPO] at a) 10^{-3} M [Cl^-] from solvent extraction, b) 10^{-3} M [Cl^-] from CPC, c) 0.1 M [Cl^-] from solvent extraction and d) 0.1 M [Cl^-] from CPC.

FIGURE 3.   Chromatogram of the separation of Pd(II) from Pt(II) at 0.1 M [Cl^-], 0.5 M [TOPO], pH = 3 and flow rate = 0.54 mL/min., a) chloride peak corresponding to dead volume, b) 10^{-3} M Pt and c) 4×10^{-3} M Pd.

FIGURE 4.   The computer simulated chromatogram of the separation of Pd(II) and Pt(II) at N = 360, D_{Pt} = 0.11 and D_{Pd} = 1.4.

FIGURE 5.   The chromatogram of the separation of Pd(II) from Pt(II), Ir(III) and Rh(III) at 0.1 M [Cl^-], 0.5 M [TOPO], pH = 3, and flow rate =0.63 mL/min., a) chloride peak corresponding to the dead volume, b) 5×10^{-4} M Ir(III) and Rh(III), c) 10^{-3} M Pt(II) and d) 4×10^{-3} M Pd.

FIGURE 6.   The efficiency of CPC as a function of flow rate for Pd(II)-TOPO system at 0.1 M [TOPO], 10^{-2} M[Cl^-] and pH = 2.